

**Resin useful for preparing an electrophotographic toner.**

Patent Number: ☐ [EP0148476, A3](#)  
Publication date: 1985-07-17  
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Requested Patent: ☐ [JP60134248](#)  
Application Number: EP19840115868 19841219  
Priority Number(s): JP19830243390 19831223  
IPC Classification: G03G9/08  
EC Classification: [G03G9/08S](#)  
Equivalents: BR8406685, ☐ [ES8706534](#)  
Cited patent(s): [US4418137](#); [NL7502493](#); [US4473628](#); [GB2078385](#); [GB2017949](#); [US4175962](#)

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**Abstract**

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A resin useful for preparing an electrophotographic toner, comprising particles of a double layer structure composed of (A) a layer of a low-temperature melting emulsion polymer having a 4 mm descending temperature of 90 to 130 DEG C and (B) a layer of a high-temperature melting-emulsion polymer having a 4 mm descending temperature of 130 to 170 DEG C, said particles of the resin having a 4 mm descending temperature of 100 to 150 DEG C. The 4 mm descending temperature is defined as the temperature at which the plunger of a flow tester descends 4 mm in a referential test set forth in JIS K-7210 under conditions involving a die diameter of 1 mm, a die length of 10 mm, a load of 100 kg/cm<sup>2</sup> and a temperature raising rate of 6 DEG C.

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European Patent Office  
Office européen des brevets

⑪ Publication number:

**0 148 476**  
**A2**

**EUROPEAN PATENT APPLICATION**

⑫ Application number: **84115868.6**

⑤① Int. Cl.: **G 03 G 9/08**

⑫ Date of filing: **19.12.84**

③① Priority: **23.12.83 JP 243390/83**

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④③ Date of publication of application: **17.07.85**  
Bulletin 85/29

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⑥④ Designated Contracting States: **DE GB NL**

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⑥④ Resin useful for preparing an electrophotographic toner.

⑥⑦ A resin useful for preparing an electrophotographic toner, comprising particles of a double layer structure composed of (A) a layer of a low-temperature melting emulsion polymer having a 4 mm descending temperature of 90 to 130°C and (B) a layer of a high-temperature melting emulsion polymer having a 4 mm descending temperature of 130 to 170°C, said particles of the resin having a 4 mm descending temperature of 100 to 150°C. The 4 mm descending temperature is defined as the temperature at which the plunger of a flow tester descends 4 mm in a referential test set forth in JIS K-7210 under conditions involving a die diameter of 1 mm, a die length of 10 mm, a load of 100 kg/cm<sup>2</sup> and a temperature raising rate of 6°C.

**EP 0 148 476 A2**

This invention relates to a resin useful for preparing a toner for developing a latent electrostatic image formed in electrophotography, particularly a toner adapted for fixation by hot rollers.

In electrophotography, a copy of a document is obtained generally by forming a latent electrostatic image corresponding to the image of the document on a photosensitive material, applying a toner composed of fine particles of a binder resin containing a coloring agent to the latent image by various means to develop it into a visible image, transferring the visible toner image to a receptor sheet such as a sheet of paper, and fixing the toner image by application of heat, pressure, a solvent vapor, etc.

The most general method of fixation now in use is a so-called hot roller fixing method utilizing heat and pressure. According to this method, an oil such as a silicone oil is coated on rollers in order to increase the releasability of the toner from the hot rollers. Coating of the oil, however, leads to various troubles owing to the complexity of the fixing device, and the gasification of the oil itself also causes various troubles. It has been desired therefore to establish a hot roller fixing method which does not require coating of oils.

Accordingly, it has been desired to develop a toner which is free from a phenomenon of adhesion to rolls (the offset phenomenon) even in the absence of an oil coating, and can be fixed well at low temperatures.

It is known that the offset phenomenon and fixability are predominantly affected by the structure of a binder resin as a constituent of the toner. Attempts have been made heretofore to improve the releasability of the toner from the rollers and the thermal properties of

the toner by the structure of the binder resin. For example, there is a method in which a low-molecular-weight olefin resin such as low-molecular-weight polypropylene is used as one component of the binder resin in order to prevent the offset phenomenon. This method, however, has the problem of filming on the photosensitive material. Attempts have been made to increase the cohesive force of the toner by increasing the molecular weight of the resin or crosslinking it. These attempts have resulted in an appreciable effect of preventing offset, but have degraded the fixability of the toner. On the other hand, attempts have been made to make the glass transition temperature ( $T_g$ ) or molecular weight of the resin relatively low by the chemical composition of the resin with a view to imparting good low-temperature fixability. A toner prepared by using such a binder resin is not feasible in practical applications because the offset phenomenon occurs at low temperatures and moreover, the toner undergoes blocking.

Although the binder resin of toners is required to have both offset resistance and fixability, but it is by no means easy to satisfy these contradictory thermal properties at the same time.

Various improvements have been attempted heretofore in order to solve the aforesaid problems.

For example, Japanese Laid-Open Patent Publications Nos. 114245/1979, 27156/1981 and 113736/1977 propose a method in which two resins having different chemical compositions and/or molecular weights, i.e. a resin melting at a relatively low temperature and a resin melting at a high temperature, are dry-blended during melt kneading. Since, however, these resins have low uniform mixability, the resulting blended resin does not simultaneously satisfy offset resistance and fixability. Particularly, when blending resins having poor compatibility, a uniform mixture is very difficult to obtain,

and the fixability of a toner prepared from the resulting resin becomes unstable.

Japanese Laid-Open Patent Publication No.

158340/1981 proposes a method in which two resins having  
5 different chemical compositions and/or molecular weights  
are produced by suspension polymerization continuously in  
two steps. However, dispersed resin particles in suspen-  
sion polymerization are generally as large as several  
hundred microns or more. Hence, the uniform mixability  
10 of the two resins is poor, and the resulting mixed resin  
does not give satisfactory thermal properties.

Japanese Patent Publication No. 150855/1982  
proposes a method in which two polymer latices having  
different characteristics obtained by emulsion polymeri-  
15 zation are blended and then co-coagulated to form a toner  
resin. This method is improved to some extent in regard  
to the uniform mixability of the two resins over the  
conventional blending methods. However, in the co-  
coagulation of polymer latices of basically different  
20 chemical compositions and molecular weights, coagulation  
of particles of the same resin occurs preferentially, and  
it is difficult to recover the product in a completely  
uniform state. Furthermore, depending upon the selection  
of the resin combination, complete separation of the two  
25 resins occurs and a uniform mixture cannot be obtained.  
Accordingly, this method can neither meet the dual re-  
quirement of fixability and offset resistance.

It is an object of this invention to overcome  
the defects of the prior art described above by providing  
30 a resin useful for preparation of an electrophotographic  
toner in which two resins having different thermal pro-  
perties are fully uniformly mixed and which has good and  
stable fixability and excellent offset resistance and can  
be fixed by hot rollers without an oil coating.

35 The above object of this invention is achieved by

a resin useful for preparing an electrophotographic toner, comprising particles of a double layer structure composed of (A) a layer of a low-temperature melting emulsion polymer having a 4 mm descending temperature of 90 to 130 °C, preferably 100 to 120 °C and (B) a layer of a high-temperature melting emulsion polymer having a 4 mm descending temperature of 130 to 170 °C, preferably 140 to 160 °C, said particles of the resin having a 4 mm descending temperature of 100 to 150 °C, preferably 110 to 140 °C, said 4 mm descending temperature being defined as the temperature at which the plunger of a flow tester descends 4 mm in a referential test set forth in JIS K-7210 under conditions involving a die diameter of 1 mm, a die length of 10 mm, a load of 100 kg/cm<sup>2</sup> and a temperature raising rate of 6 °C.

The resin particles of a double layer structure composed of the low-temperature melting resin layer and the high-temperature melting resin layer can be obtained by emulsion polymerizing a monomeric material for either one of the two resins in the presence of a latex of the other resin by an ordinary seed polymerization method. The resulting resin latex particles are unitary minute latex particles in which the monomeric material for one of the resins is polymerized and covers the surface of the minute particles of the other resin and the two resins are firmly bonded physically or chemically at their interface. In a subsequent coagulation treatment, therefore, the two resins do not separate from each other and a very uniform mixed resin can be obtained. By melt-kneading the mixed resin with a coloring gent, etc. a toner having a completely uniform composition and properties can be obtained. Furthermore, the energy required for kneading can be drastically reduced.

Since the low-temperature melting resin portion betters the fixability of the toner and the high-temperature melting resin portion maintains good offset

resistance, fixability and offset resistance, which are contradictory thermal properties, can be maintained in good balance by the use of the resin of this invention. More specifically, there is a large difference between  
5 the lowest temperature at which the toner can be fixed and the lowest temperature at which the offset phenomenon of the toner occurs (i.e., a broad fixable temperature range), and the toner exhibits excellent fixability even when fixed by hot rollers not coated with an oil. If the  
10 4 mm descending temperatures of the low-temperature melting resin portion, the high-temperature melting resin portion and the double-layered particles are below the above-specified lower limits, offset tends to occur. If they are higher than the upper limits, the fixation of  
15 the toner becomes poor and the toner is of no practical use.

The temperature at which the resin begins to flow in the referential test of JIS K-7210 is desirably 60 to 100 °C for the low-temperature melting resin  
20 portion, 100 to 140 °C for the high-temperature melting resin portion, and 80 to 130 °C for the double-layered resin particles.

A resin mixture prepared by methods other than the seed polymerization method, for example simple dry-  
25 blending, solution blending or latex blending, does not comprise particles of a double layer structure, and therefore cannot give a sufficient fixable temperature range. Moreover, a toner prepared from it has unstable fixability.

30 The thermal properties of the resin in accordance with this invention is determined by its composition, molecular weight, crosslinked structure, etc. Introduction of a crosslinked structure into the high-temperature melting resin portion is an effective means.

35 Various monomers can be used for producing the individual resin layers, but typically vinyl compounds

are used. Examples of the vinyl compounds include styrene compounds such as styrene, vinyltoluene and alpha-methylstyrene; (meth)acrylic acid and derivatives thereof, such as acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, acrylonitrile and acrylamide; ethylenically unsaturated monolefins such as ethylene, propylene and butylene; diolefins such as butadiene, isoprene and piperylene; vinyl halides such as vinyl chloride, vinylidene chloride and vinyl fluoride; vinyl esters such as vinyl acetate and vinyl propionate; vinyl ethers such as vinyl methyl ether and vinyl ethyl ether; vinyl ketones such as vinyl methyl ketone and methyl isopropenyl ketone; and nitrogen-containing vinyl compounds such as 2-vinylpyridine, 1-vinylpyridine and N-vinylpyrrolidone. These vinyl compounds may be used singly or in combination. The use of styrene alone or a mixture of a major proportion of styrene and a minor proportion of (meth)acrylic acid or its derivative or a diolefin is preferred. From the viewpoint of pulverizability, polymers or copolymers from these monomers are recommended either as the low-temperature melting resin or as the high-temperature melting resin.

A general technique for introducing a cross-linked structure into the resin is to perform the polymerization of the monomers in the presence of a crosslinking agent added. Examples of the crosslinking agent include aromatic divinyl compounds such as divinylbenzene, divinyl-naphthalene and the derivatives thereof; diethylenically unsaturated carboxylic acid esters such as ethylene glycol dimethacrylate and diethylene glycol dimethacrylate; divinyl compounds such as N,N-divinylaniline

and divinyl ether; and compounds having at least three vinyl groups. These crosslinking compounds may be used singly or in combination.

5 The molecular weight of the resin can be freely determined by adding an arbitrary amount of a molecular weight controlling agent such as t-butylmercaptan or dodecylmercaptan in the process of producing the resin.

10 Any desired surface-active agents can be used in emulsion polymerization. Examples include anionic soaps such as sodium alkylbenzenesulfonates, sodium salts of higher alcohol sulfate esters, or sodium or potassium salts of higher fatty acids; nonionic soaps such as polyethylene glycol ether; and cationic soaps such as dodecylamine hydrochloride.

15 The seed polymerization is carried out by known procedures. However, the concentration of the surface-active agent in the polymerization system during the polymerization in the second step performed after the termination of the polymerization in the first step,  
20 should be such that the polymer formed in the second step fully covers the polymer particles formed in the first step.

Generally, a water-soluble or oil-soluble polymerization initiator is used. Examples of preferred  
25 polymerization initiators are persulfate salts such as potassium persulfate, hydroperoxides such as cumene hydroperoxide and para-menthane hydroperoxide, and redox systems.

30 In the production of the toner resin in accordance with this invention, another resin may be mixed with the emulsion polymer obtained by seed polymerization in an amount which does not impair the object of this invention. Examples of the other resin include polyester resins, epoxy resins, polyurethane resins, and polyether  
35 resins.

As stated above, the toner resin in accordance

with this invention can be produced by a polymerization process without the need for complex steps in the prior art such as dry blending or solution blending.

In preparing a toner from the resin of this invention as a binder, there can be used any desired pigment such as titanium dioxide, silicon dioxide, zinc oxide and carbon black, and any desired magnetic powders such as magnetic powders of iron, cobalt, nickel, iron sesquioxide, triiron tetroxide, manganese iron oxide, zinc iron oxide and nickel iron oxide. To control the charge of the toner, a dye such as nigrosine base, aniline blue, chrome yellow, ultramarine blue, orient oil red, phthalocyanine blue and malachite green oxalate may be used as required.

The particle diameter required of the toner is generally about 2 to 50 microns. The toner can be prepared by thoroughly mixing the above resin, the pigment, the dye, etc. by melt kneading under heat for example, and pulverizing the mixture by an ordinary pulverizer such as as hammer mill or a jet mill.

The resulting toner composition containing the resin of this invention has excellent toner properties. It exhibits better fixability than conventional toner compositions even in a high-speed copying apparatus or when it is fixed by the hot roller fixing method, and can give clear images free from the offset phenomenon.

The following examples illustrate the present invention more specifically. All parts in these examples are by weight.

30

#### EXAMPLE 1

A polymerization reactor equipped with a stirrer was charged with 70 parts of deionized water, 0.45 part of sodium laurylsulfate and 0.05 part of sodium carbonate, and with stirring, a mixture composed of 24 parts of styrene, 6 parts of butyl acrylate and 0.01 part of t-dodecylmercaptan was added and emulsified. The

polymerization system was then fully deaerated and purged with nitrogen. With stirring, the temperature of the polymerization system was raised to 50 °C. Potassium persulfate (0.1 part) was added to initiate the polymerization. In 12 hours after the initiation of the polymerization, the polymerization was completed to obtain a first-stage polymer latex.

To the polymerization system in which the polymer latex was present, 150 parts of deionized water, 0.6 part of sodium laurylsulfate and 0.09 part of sodium carbonate were added. Further, 56 parts of styrene, 14 parts of butyl acrylate and 1.0 part of t-dodecylmercaptan were added. They were mixed with stirring so that the polymerization system became uniform. Then, 0.2 part of potassium persulfate was added, and the reaction was carried out at 50 °C for 10 hours to complete the second-stage polymerization.

The emulsion was salted out, filtered, and dried to obtain a resin. The resin had a 4mm descending temperature of 120 °C.

The 4 mm descending temperatures of resin (A) obtained by salting out and drying the first-stage polymer latex and a resin (B) obtained by performing polymerization separately in accordance with the polymerization recipe and conditions in the second stage were measured. The results are shown in the following table.

One hundred parts of the resin obtained by the above seed polymerization method was mixed with 10 parts of carbon black and the mixture was melt-kneaded by two hot rolls and finely pulverized by a jet mill. The fine powder was classified by wind to obtain a toner having an average particle diameter of 15 microns.

A developer was prepared by mixing the toner with an iron powder carrier. A latent electrostatic image was formed on a selenium photosensitive material by an ordinary electrophotographic process and developed

with the developer. The developed image was transferred to plain paper by corona discharge and heat fixed by silicon-Teflon hot rollers. As shown in the following table, the tone had a low lowest fixable temperature (Tf), a high lowest offset generating temperature ( $T_{HO}$ ), and a broad fixable temperature range ( $T_{HO} - Tf$ ). Accordingly, the toner had good fixability and offset resistance.

The Tf and  $T_{HO}$  were measured as follows:-

10 The surface temperature of hot fixing rollers (that roller which faced the image surface was a Teflon rubber roller) was kept at a fixed point, and a solid image transferred to plain paper was passed between the rollers. The surface temperature of the rollers was  
15 changed at 10°C intervals, and the phenomenon in which the toner adhering to the roller was again transferred to the white portion of the same paper (offset phenomenon) was observed. The lowest temperature at which the offset phenomenon occurred was defined as the lowest offset  
20 generating temperature  $T_{HO}$ . As regards fixability, the solid image was rubbed with a friction member having a sanded rubber eraser by reciprocating it over the solid image through 5 cycles, and thereafter the density of the image was compared with that before rubbing. When the  
25 image density was at least 70% of that before rubbing, it was judged that the toner was fixed. The lowest temperature at which the fixation was effected was defined as Tf.

#### COMPARATIVE EXAMPLE 1

30 A resin was prepared by seed polymerization in the same way as in Example 1 except that in the second-stage polymerization, 49 parts of styrene, 21 parts of butyl acrylate and 3.5 parts of 1-dodecylmercaptan were used.

35 A toner was prepared by using the resulting resin in the same way as in Example 1, and tested for

fixability. As shown in the following table, this toner had poor offset resistance and a narrow fixable temperature range, and did not have properties suitable for practical application.

#### EXAMPLE 2

5 A polymerization reactor equipped with a stirrer was charged with 50 parts of deionized water, 0.5 part of sodium dodecylbenzenesulfate and 0.04 part of sodium carbonate. With stirring, a mixture composed of  
10 17.5 parts of styrene, 7.5 parts of butyl acrylate, 0.11 part of divinylbenzene and 0.04 part of 1-dodecylmercaptan was added and emulsified. Then, by the same method as in Example 1, a first-stage polymer latex was obtained.

15 A dispersion composed of 150 parts of deionized water, 0.1 part of sodium dodecylbenzenesulfate, 0.1 part of naphthalene/sodium sulfate condensate, 60 parts of styrene, 15 parts of butyl methacrylate and 1.4 parts of t-dodecylmercaptan was added to the polymerization system  
20 in which the above polymer latex was present, and the second-stage polymerization was completed by the same method as in Example 1. The resulting emulsion was salted out, filtered and dried to obtain a resin.

One hundred parts of the resulting resin was  
25 mixed with 3 parts of a nigrosine-type dye and 80 parts of magnetite. They were melt-kneaded, finely pulverized by a jet mill and classified by wind to give a magnetic toner having an average particle diameter of 10 microns.

The toner was tested for fixability by the same  
30 method as in Example 1, and was found to show good fixability and offset resistance as shown in the following table.

#### COMPARATIVE EXAMPLE 2

The resin powder obtained by the first-stage  
35 polymerization in Example 1 and a resin powder obtained by separately performing polymerization in accordance

with the recipe and conditions of the second-stage polymerization of Example 2 were melt-kneaded in a weight ratio of 1:3, and then a magnetic toner having an average particle diameter of 10 microns was prepared by using the  
5 resulting resin in the same way as in Example 2.

The toner was tested for fixability. It was found as shown in the following table that the toner could be fixed at a relatively low temperature, but showed a low offset generating temperature and a narrow  
10 fixable temperature range. Such a toner cannot be satisfactorily used for practical applications.

#### COMPARATIVE EXAMPLE 3

The first-stage polymer latex obtained in Example 2 was blended with a polymer latex separately  
15 prepared in accordance with the same polymerization recipe and under the same polymerization conditions as in the second-stage polymerization in Example 2 except that 0.7 part of sodium dodecylbenzenesulfate was used. The blend was salted out, filtered, and dried to obtain a  
20 resin. A magnetic toner having an average particle diameter of 13 microns was prepared by using this resin by the same method as in Example 2. When the toner was tested for fixability, it was found to have poor offset resistance as shown in the following table.

#### COMPARATIVE EXAMPLE 4

A solution of 0.05 part of polyvinyl alcohol in 100 parts of deionized water was put into a polymerization reactor equipped with a stirrer and a baffle. Then, 17.5 parts of styrene, 7.5 parts of butyl acrylate, 0.11  
30 part of divinylbenzene, 0.03 part of azobisisobutyronitrile and 0.03 part of 1-butylmercaptan were added and suspended. Then, the inside of the reactor was fully deaerated and purged with nitrogen. With stirring, the temperature of the inside of the reactor was raised to 70  
35 °C, and the first-stage polymerization was completed in 10 hours.

The polymerization system was cooled to 40 °C, and a mixture of 60 parts of styrene, 15 parts of butyl methacrylate, 0.1 part of azobisisobutyronitrile and 0.9 part of t-butylmercaptan was added. Furthermore, 5 200 parts of water having 0.15 part of polyvinyl alcohol dissolved in it was added. The mixture was fully stirred, and the temperature of the inside of the reactor was raised to 70 °C. The second-stage polymerization was completed in 15 hours. The polymerization system was 10 then cooled, dehydrated, washed repeatedly with water, and dried to obtain a resin.

A toner was prepared from the resulting resin in the same way as in Example 2, and tested for fixability. As shown in the following table, it had poor 15 offset resistance.

#### COMPARATIVE EXAMPLE 5

The same polymerization as the first-stage polymerization in Example 2 was performed except that the polymerization recipe was changed to 16 parts of styrene, 20 5 parts of butyl acrylate, 4 parts of acrylonitrile, 0.4 part of divinylbenzene and 0.03 part of 1-dodecylmercaptan. Subsequently, the second-stage polymerization was carried out in accordance with the same polymerization recipe and under the same polymerization con- 25 ditions as in Example 2 to obtain a resin.

A toner was prepared from the resulting resin in the same way as in Example 2, and tested for fixability. As shown in the following table, it had a high 30 lowest fixable temperature, and could not be used in practical applications.

#### EXAMPLE 3

A polymerization reactor equipped with a stirrer was charged with 58 parts of deionized water, 0.5 part of potassium oleate and 0.04 part of sodium carbonate. With stirring, a mixture composed of 17 parts of 35 styrene, 8 parts of 2-ethylhexyl acrylate, 0.58 part of

ethylene glycol dimethacrylate and 0.1 part of t-butylmercaptan was added and emulsified. Thereafter, by the same way as in Example 1, a first-stage polymer latex was obtained.

5           To the polymerization system in which the above polymer latex was present, a dispersion composed of 170 parts of deionized water, 0.8 part of potassium oleate, 61 parts of styrene, 11 parts of 2-ethylhexyl acrylate and 1.2 parts of t-butylmercaptan was added. Then, by  
10 the same method as in Example 1, the second-stage polymerization was completed. The resulting emulsion was salted out, filtered, and dried to obtain a resin.

One hundred parts of the resulting resin was mixed with 5 parts of a gold-containing dye and 100 parts  
15 of magnetite, and the mixture was melt-kneaded, finely pulverized and classified to give a magnetic toner having an average particle diameter of 12 microns. The toner was tested for fixability by the same method as in Example 1. As shown in the following table, it exhibited  
20 good fixability and offset resistance.

COMPARATIVE EXAMPLE 6

A polymerization reactor was charged with 116 parts of deionized water, 1.0 part of potassium oleate and 0.08 part of sodium carbonate. With stirring, a  
25 mixture of 35 parts of styrene, 15 parts of 2-ethylhexyl acrylate, 0.7 part of ethylene glycol dimethacrylate and 0.1 part of t-butylmercaptan was added. Then, by the same method as in Example 1, a first-stage polymer latex was obtained.

30           To the polymerization system in which the polymer latex was present, a dispersion composed of 114 parts of deionized water, 0.33 part of potassium oleate, 43 parts of styrene, 7 parts of 2-ethylhexyl acrylate and 0.7 part of t-butylmercaptan was added. Then, by the  
35 same method as in Example 1, the second-stage polymerization as completed. The emulsion was salted out,

- 15 -

filtered and dried to obtain a resin.

A toner was prepared from the resin by the same method as in Example 3, and tested for fixability. As shown in the following table, it had a high lowest  
5 fixable temperature and could not be used in practical applications.

#### EXAMPLE 4

A polymerization reactor equipped with a stirrer was charged with 180 parts of deionized water, 1.2  
10 parts of potassium oleate and 0.12 parts of sodium carbonate. With stirring, 12 parts of butyl acrylate, 678 parts of styrene and 1.5 parts of t-dodecylmercaptan were added, and by the same method as in Example 1, a first-stage polymer latex was obtained.

15 To the polymerization system in which the polymer latex was present was added a dispersion composed of 16 parts of deionized water, 0.2 part of potassium oleate, 17 parts of styrene, 3 parts of butadiene, 0.14 part of vinylbenzene and 0.05 part of t-dodecylmercaptan.  
20 Then, by the same method as in Example 1, the second-stage polymerization was completed. The emulsion was salted out with calcium chloride, and dried to obtain a resin.

One hundred parts of the resulting resin was  
25 mixed with 4 parts of a nigrosene-type dye and 100 parts of magnetite. The mixture was melt kneaded, finely pulverized and classified to obtain a magnetic toner having an average particle diameter of 13 microns. The toner was tested for fixability in the same way as in  
30 Example 1. As shown in the following example, it had excellent offset resistance and good fixability.

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Table

Example (Ex.) or Comparative Example (CEX.)	4mm Descending temperature (°C)			Weight ratio of the first-stage polymer to the second-stage polymer	Properties of the toner		
	First- stage polymer	Second- stage polymer (*)	Final polymer		Lowest fixable temperature (T <sub>f</sub> , °C)	Lowest offset generating temperature (T <sub>HO</sub> , °C)	Fixable temperature range (T <sub>HO</sub> - T <sub>f</sub> , °C)
Ex. 1	145	113	120	30/70	140	220	80
CEX. 1	145	85	115	30/70	120	145	25
Ex. 2	149	110	130	25/75	145	230	85
CEX. 2	149	110	120	25/75 (dry blending)	135	150	15
CEX. 3	149	110	125	25/75 (latex blend- ing)	140	170	30
CEX. 4	148	109	123	25/75 (suspension polymerization)	130	160	30
CEX. 5	180	110	143	25/75	180	220	40
Ex. 3	152	112	137	25/75	148	230	82
CEX. 6	165	120	160	50/50	170	200	30
Ex. 4	105	157	140	80/20	150	240	90

(\*): The polymer was separately prepared in accordance with the same recipe as in the second-stage polymerization.

What is claimed is:

1. A resin useful for preparing an electrophotographic toner, comprising particles of a double layer structure composed of (A) a layer of a low-temperature melting emulsion polymer having a 4 mm descending temperature of 90 to 130 °C and (B) a layer of a high-temperature melting emulsion polymer having a 4 mm descending temperature of 130 to 170 °C, said particles of the resin having a 4 mm descending temperature of 100 to 150 °C, said 4 mm descending temperature being defined as the temperature at which the plunger of a flow tester descends 4 mm in a referential test set forth in JIS K-7210 under conditions involving a die diameter of 1 mm, a die length of 10 mm, a load of 100 kg/cm<sup>2</sup> and a temperature raising rate of 6 °C.
2. The resin of claim 1 wherein the emulsion polymer of each of the layers (A) and (B) is a polymer of a vinyl compound.
3. The resin of claim 2 wherein the polymer of a vinyl compound is a homopolymer of a styrene compound or a copolymer containing a major proportion of a styrene compound.
4. The resin of claim 1 wherein the high-melting emulsion polymer layer (B) has a crosslinked structure.
5. The resin of claim 1 wherein the particles of a double layer structure are composed of an inner layer of the high-temperature melting emulsion polymer layer (B) and an outer layer of the low-temperature melting emulsion polymer layer (A).
6. The resin of claim 1 wherein the particles of a double layer structure are prepared by a seed polymerization method.



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

Publication number:

**0 148 476**  
**A3**

**EUROPEAN PATENT APPLICATION**

Application number: **84115868.6**

Int. Cl.<sup>4</sup>: **G 03 G 9/08**

Date of filing: **19.12.84**

Priority: **23.12.83 JP 243390/83**

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Designated Contracting States: **DE GB NL**

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Date of deferred publication of search report: **30.10.85 Bulletin 85/44**

**Resin useful for preparing an electrophotographic toner.**

A resin useful for preparing an electrophotographic toner, comprising particles of a double layer structure composed of (A) a layer of a low-temperature melting emulsion polymer having a 4 mm descending temperature of 90 to 130°C and (B) a layer of a high-temperature melting emulsion polymer having a 4 mm descending temperature of 130 to 170°C, said particles of the resin having a 4 mm descending temperature of 100 to 150°C. The 4 mm descending temperature is defined as the temperature at which the plunger of a flow tester descends 4 mm in a referential test set forth in JIS K-7210 under conditions involving a die diameter of 1 mm, a die length of 10 mm, a load of 100 kg/cm<sup>2</sup> and a temperature raising rate of 6°C.

**EP 0 148 476 A3**



European Patent  
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# EUROPEAN SEARCH REPORT

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EP 84 11 5868

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-4 418 137 (MITSUHASHI et al.) ---		G 03 G 9/08
A	NL-A-7 502 493 (XEROX) ---		
P, A	US-A-4 473 628 (TAKAHIRA KASUYA et al.) & JP - A - 57 150 855 (Cat. D, A) ---		
A	GB-A-2 078 385 (KONISHIROKU) & JP - A - 56 158 340 (Cat. D, A) ---		
A	GB-A-2 017 949 (FUJI XEROX) & JP - A - 54 114 245 (Cat. D, A) ---		
A	US-A-4 175 962 (SHIGERU SADAMATSU) & JP - A - 52 113 736 (Cat. D, A) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-07-1985	Examiner AMAND J. R. P.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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